

## Apatites of Divalent Europium\*

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The preparation methods of  $\text{Eu}_3(\text{PO}_4)_2$ ,  $\text{Eu}_5(\text{PO}_4)_3\text{F}$ ,  $\text{Eu}_3(\text{PO}_4)\text{Cl}$  and  $\text{Eu}_5(\text{AsO}_4)_3\text{OH}$  are described.  $\text{Eu}_3(\text{PO}_4)_2$  crystallizes in a rhombohedral unit cell and the apatite like compounds in the  $P6_3/m$  hexagonal structure. All the compounds are isomorphous with the corresponding Sr compounds, and similar in size. Magnetic susceptibility measurements show that  $\text{Eu}_3(\text{PO}_4)_2$  is magnetically ordered below 5 K and  $\text{Eu}_5(\text{PO}_4)_3\text{F}$  and  $\text{Eu}_5(\text{PO}_4)_3\text{Cl}$  are paramagnetic. Solid solution of the  $\text{Eu}_{5-x}\text{Ca}_x(\text{PO}_4)_3\text{F}$  system obey Vegard's law, while the  $\text{Eu}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{F}$  and  $\text{Eu}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{Cl}$  systems show a trend to form ordered solid solutions.

Apatites have the general formula  $\text{M}_5(\text{XO}_4)_3\text{YV}$  and they occur both in natural and synthetic form, with a large variety of ions. The apatites investigated include those in which M stands for the alkaline earth, Pb and Cd metals, X for P, As, V, Mn, Cr, Si and Ge and Y for F, Cl and OH. Rare earth metals were also found as cations in apatites, as dopants or as one of the metal ions in silicate apatites. Recently, the substitution of rare earth ions in alkaline earth apatites has been studied (1).

Apatites can be well characterized by their crystal structure. Fluoride apatites have a hexagonal unit cell with two formula units in each cell (2). The ten metal ions are located in two nonequivalent crystallographic sites, four of them along the threefold axes and the other six, symmetrically located about the sixfold screw axes. Hydroxy and chloride apatites have monoclinic unit cells, a distorted version of the hexagonal apatite (3, 4). The rather large Cl ions are displaced from the planes of the triangles formed by the  $\text{M}_{11}$  ions and they are approximately halfway between the  $\text{M}_{11}$  triangles.

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Among the rare earth elements europium forms the most stable divalent ion. In its properties,  $\text{Eu}^{2+}$  shows much similarity to the alkaline earths and therefore the formation of apatite like compounds by  $\text{Eu}^{2+}$  can be expected. In fact, the existence of  $\text{Eu}_5(\text{PO}_4)_3\text{-OH}$  and  $\text{Eu(II)-silicate}$  apatites have been already reported (5, 6).

$\text{Eu}^{2+}$  has magnetic properties quite different from  $\text{Eu}^{3+}$ . The ionic ground state of  $\text{Eu}^{2+}$  ( $4f^7$ ) is  $^8\text{S}_{7/2}$  and that of  $\text{Eu}^{3+}$  ( $4f^6$ ) is  $^7\text{F}_0$ , which is diamagnetic. Mössbauer effect studies have shown very large isomer shifts between  $\text{Eu(II)}$  and  $\text{Eu(III)}$  compounds when studied with 21.6 keV  $\gamma$ -rays of  $\text{Eu}^{151}$ . Divalent Eu compounds have an isomer shift between  $-8.7$  and  $-14.5$  mm/sec relative to  $\text{Eu}_2\text{O}_3$ , while trivalent Eu compounds have an isomer shift between  $-1.0$  and  $+3.6$  mm/sec relative to  $\text{Eu}_2\text{O}_3$  (7, 8). Mössbauer effect and magnetic measurements are therefore useful tools in determining the valency of Eu in its compounds.

The examination of the environment of the alkali and alkali earth cations in biological systems is of great importance. Advanced physical techniques can be applied for these purposes only, when paramagnetic ions replace the alkali and alkaline earth ions. The replace-

ment will be effective when it is isomorphous and therefore the substituted ions must be of similar size. Many of the rare earths satisfy these requirements, but  $\text{Eu}^{2+}$  appears to be especially useful because in addition to being paramagnetic it is also a Mössbauer nuclide.

In the present paper the preparation of  $\text{Eu}_3(\text{PO}_4)_2$  and the apatites of divalent europium is described together with crystal and magnetic data of these compounds. Solid solutions of the Eu(II)-apatites were also prepared and studied by the above methods.

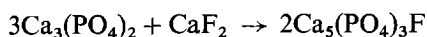
## Experimental

### 1. Preparation of the Starting Materials

(a)  $\text{EuF}_2$ . This compound was prepared by treating ~2 gr  $\text{EuSO}_4$  in 300 ml of boiling solution of 0.4 *N* NaOH with 0.5 *M* NaF for 2 hr under argon atmosphere (9).  $\text{EuSO}_4$  was prepared by dissolving  $\text{Eu}_2\text{O}_3$  in HCl and passing the solution through a Jones reductor into 8*N*  $\text{H}_2\text{SO}_4$  (10).

(b)  $\text{EuCl}_2$ . The preparation of this compound was described by Howell and Pytlewski (11). It consists of dissolving metallic europium in liquid ammonia with  $\text{NH}_4\text{Cl}$ .

(c) *Calcium and barium apatite*.  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  was synthesized by the solid state reaction.



The well dried reagents were preheated at 700°C for 2 hr and heated at 1000°C for 2 hr.

The fluoro and chloroapatites of Ba were prepared by heating  $\text{BaHPO}_4$ ,  $\text{BaCO}_3$  and  $\text{BaF}_2$  or  $\text{BaCl}_2$  under argon atmosphere at 1100°C.

### Preparation of Solid Solutions

Three series of solid solutions were prepared:

(I)  $\text{Eu}_{5-x}\text{Ca}_x(\text{PO}_4)_3\text{F}$ ; (II)  $\text{Eu}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{F}$  and (III)  $\text{Eu}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{Cl}$  ( $0 \leq x \leq 5$ )

The compositions in system (I) were prepared by heating mixtures of  $\text{Eu}_3(\text{PO}_4)_2$ ,  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{EuF}_2$ . The solid solutions in the (II) and (III) systems were prepared by reacting the fluoride and chloride apatites of

Ba with that of Eu (II). The above solid state reactions were carried out under conditions similar to the preparation of the pure Eu (II) apatites.

The purity of the samples was determined by an analysis of their powder X-ray diffraction patterns. The X-ray patterns were taken by a Philips Diffractometer using Ni filtered  $\text{CuK}\alpha$  radiation. The lattice constants were calculated by a least square refinement program.

Mössbauer spectra were taken by an equipment described elsewhere (12). The source used was  $\text{Sm}^{151}$  in the form of  $\text{Sm}_2\text{O}_3$ . The energy of the  $\gamma$ -rays was 21.6 keV.

Magnetic measurements were made between 4.2 and 70 K at magnetic fields of 2–15 kOe by a Null Coil pendulum magnetometer (13).

IR spectra were recorded on a Perkin Elmer grating spectrophotometer, using KBr pellets.

## Results

### 1. Preparation Methods of Divalent Europium Phosphates and $\text{Eu}_5(\text{AsO}_4)_3\text{OH}$

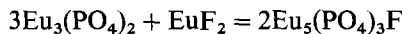
(a)  $\text{Eu}_3(\text{PO}_4)_2$ . Attempts to prepare this compound in solution, by adding  $\text{EuCl}_2$  to a solution of  $\text{H}_3\text{PO}_4$  or  $\text{Na}_2\text{HPO}_4$  and also by treating  $\text{EuCO}_3$  with a solution of  $\text{H}_3\text{PO}_4$ , failed. When  $\text{EuO}$  was reacted at 1000°C with  $\text{P}_2\text{O}_5$ ,  $\text{Eu}_3(\text{PO}_4)_2$  was obtained, but despite all the precautions to avoid oxidation, traces of  $\text{Eu}^{3+}$  were always found in it.  $\text{Eu}_3(\text{PO}_4)_2$  was finally prepared by the reduction of  $\text{EuPO}_4$  by metallic Eu as follows:



The starting materials were taken in an amount sufficient for the preparation of 500 mg  $\text{Eu}_3(\text{PO}_4)_2$ . The amount of Eu metal used was 1.2–1.4 times the stoichiometric amount. Small pieces of Eu metal were introduced together with  $\text{EuPO}_4$  into a quartz tube (9 mm diameter) and closed under vacuum. The tube was heated for a period of 20 hours in an electric furnace. The temperature at the reaction site was 1000°C.  $\text{Eu}_3(\text{PO}_4)_2$  obtained by this method had a light green color. Excess of Eu could be removed mechanically.

(b)  $\text{Eu}_5(\text{PO}_4)_3\text{F}$  and  $\text{Eu}_5(\text{PO}_4)_3\text{Cl}$ .  $\text{Eu}_3(\text{PO}_4)_2$  served as starting material for the above two

compounds according to the following reactions:



The reactions were performed in vitreosil tubes, evacuated and sealed off. The heating was generally at 1000°C about 24 hr.

(c)  $\text{Eu}_5(\text{AsO}_4)_3\text{OH}$ . This compound was prepared by boiling  $\text{EuSO}_4$  under Ar atmosphere with a solution containing an excess of  $\text{Na}_2\text{HAsO}_4$  and strongly basic with  $\text{NaOH}$ . The product was filtered, washed in acetone and dried in a dessicator, and had yellow colour. It has to be kept closed to avoid oxidation.

2. X-ray Diffraction Data

Sharp and well defined powder diffraction patterns were obtained for all the compounds, indicating their good crystallization. Partial powder data of  $\text{Eu}_3(\text{PO}_4)_2$  and  $\text{Eu}_5(\text{PO}_4)_3\text{F}$  are given in Tables I and II. Examination of the powder data of  $\text{Eu}_3(\text{PO}_4)_2$  shows that this compound crystallizes in a rhombohedral structure and is isomorphous with  $\text{Sr}_3(\text{PO}_4)_2$ . The patterns of  $\text{Eu}_5(\text{PO}_4)_3\text{F}$ ,  $\text{Eu}_5(\text{PO}_4)_3\text{Cl}$  and  $\text{Eu}_5(\text{AsO}_4)_3\text{OH}$  could be indexed on the basis of a hexagonal cell and they appear to be

TABLE I

PARTIAL POWDER DIFFRACTION DATA OF  $\text{Eu}_3(\text{PO}_4)_2$ .  
HEXAGONAL INDEXING

Index of reflection <i>h k l</i>	$d_{\text{obs}}$ Å	$d_{\text{calc}}$ Å	$I_0$
1 0 1	4.543	4.541	18
0 1 2	4.212	4.221	3
1 0 4	3.390	3.397	20
0 1 5	3.017	3.022	100
1 1 0	2.694	2.693	90
1 0 7	2.417	2.421	2
0 2 1	2.315	2.316	5
2 0 2	2.270	2.270	9
0 0 9	2.201	2.203	12
0 2 4	2.111	2.111	18
1 1 6	2.089	2.088	3
2 0 5	2.011	2.011	45
1 0 1	1.824	1.824	25

TABLE II

PARTIAL POWDER DIFFRACTION DATA OF  $\text{Eu}_5(\text{PO}_4)_3\text{F}$

Index of reflection <i>h k l</i>	$d_{\text{obs}}$ Å	$d_{\text{calc}}$ Å	$I_0$
1 1 0	4.858	4.863	5
2 0 0	4.206	4.218	14
1 1 1	4.037	4.040	12
{ 2 0 1	3.633	3.643	10
{ 0 0 2			
1 0 2	3.333	3.334	30
2 1 0	3.181	3.184	20
{ 1 1 2	2.914	2.910	100
{ 2 1 1			
3 0 0	2.807	2.808	30
2 0 2	2.748	2.750	4
{ 1 0 3	2.334	2.327	5
{ 3 1 0			
{ 3 0 2	2.221	2.221	3
{ 3 1 1			

isomorphous with the  $P6_3/m$  apatite structure. The lattice constants of the compounds are listed in Table III.

The powder diffraction data of three series of solid solutions were recorded:  $\text{Eu}_{5-x}\text{Ca}_x(\text{PO}_4)_3\text{F}$ ;  $\text{Eu}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{F}$  and  $\text{Eu}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{Cl}$  ( $0 \leq x \leq 5$ ). In Figs 1, 2 and 3 the

TABLE III

CRYSTAL SYSTEM AND LATTICE CONSTANTS OF  $\text{Eu}_3(\text{PO}_4)_2$  AND  $\text{Eu}(\text{II})$  APATITES

Compound	Crystal system	Lattice constants Å	
		<i>a</i>	<i>c</i>
$\text{Eu}_3(\text{PO}_4)_2$	Hexagonal indexing	5.387(1)	19.831(4) <sup>a</sup>
	Rhombohedral indexing	7.302	$\alpha = 43^\circ 17'$
$\text{Eu}_5(\text{PO}_4)_3\text{F}$	Hexagonal	9.726(3)	7.265(5) <sup>a</sup>
$\text{Eu}_5(\text{PO}_4)_3\text{Cl}$	Hexagonal	9.866(3)	7.187(2)
$\text{Eu}_5(\text{AsO}_4)_3\text{OH}$	Hexagonal	9.995(2)	7.345(2)

<sup>a</sup> Numbers in parentheses are the standard deviations.

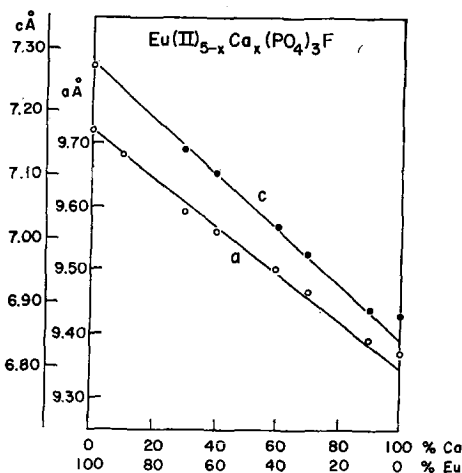


FIG. 1. Lattice constants  $a$  and  $c$  vs composition in the  $\text{Eu}_{5-x}\text{Ca}_x(\text{PO}_4)_3\text{F}$  system.

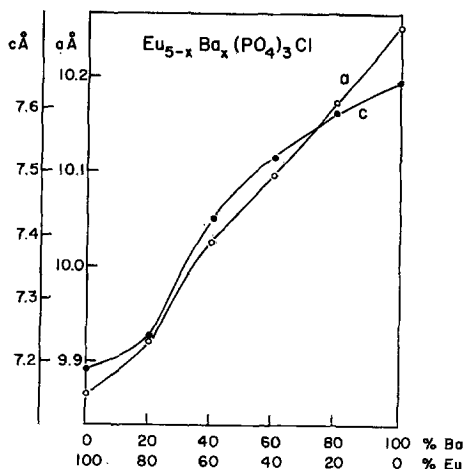


FIG. 3. Lattice constants  $a$  and  $c$  vs composition in the  $\text{Eu}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{Cl}$  system.

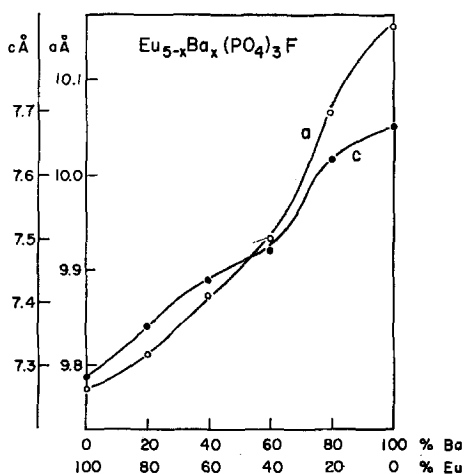


FIG. 2. Lattice constants  $a$  and  $c$  vs composition in the  $\text{Eu}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{F}$  system.

lattice constants of the solid solutions were plotted vs the composition.

### 3. Mössbauer Effect and Magnetic Data

Mössbauer spectra of all the compounds showed only one absorption maximum with an isomer shift of  $-14.0$  mm/sec. That is, the Eu in the compounds was completely in the divalent state. In the case of  $\text{Eu}_3(\text{PO}_4)_2$  Mössbauer spectrum taken at 4.2 K has shown magnetic ordering of the compounds.

The magnetization vs the temperature of  $\text{Eu}_3(\text{PO}_4)_2$ ,  $\text{Eu}_5(\text{PO}_4)_3\text{F}$  and  $\text{Eu}(\text{PO}_4)_3\text{Cl}$  are

given in Figs 4, 5 and 6. From the magnetization curve of  $\text{Eu}_3(\text{PO}_4)_2$  (Fig. 4) it can be seen that this compound is magnetically ordered with a transition temperature of  $\sim 5$  K. The measurements at 4.2 K show that this compound is magnetically saturated at a field of 12.5 kOe and the estimated saturation magnetization is  $4.4 \mu_B$ .  $\text{Eu}_5(\text{PO}_4)_3\text{F}$  and  $\text{Eu}_5(\text{PO}_4)_3\text{Cl}$  are paramagnetic at all temperatures measured. The effective moments ( $\mu_{\text{eff}}$ ) were calculated for the above three

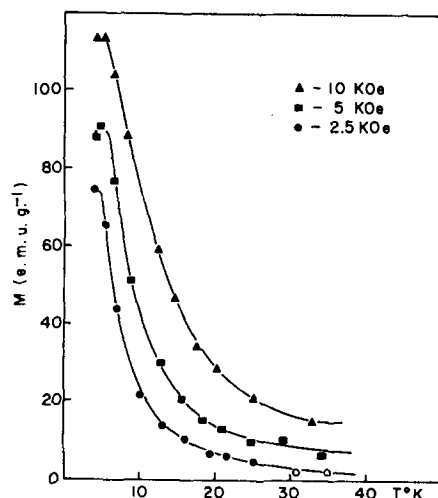


FIG. 4. Magnetic susceptibility vs temperature of  $\text{Eu}_3(\text{PO}_4)_2$ .

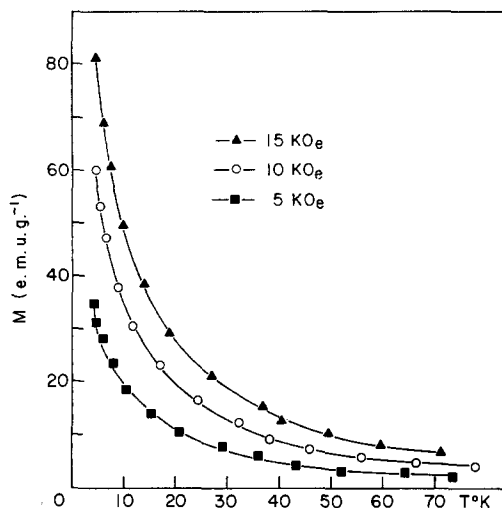


FIG. 5. Magnetic susceptibility vs temperature of  $\text{Eu}_5(\text{PO}_4)_3\text{F}$ .

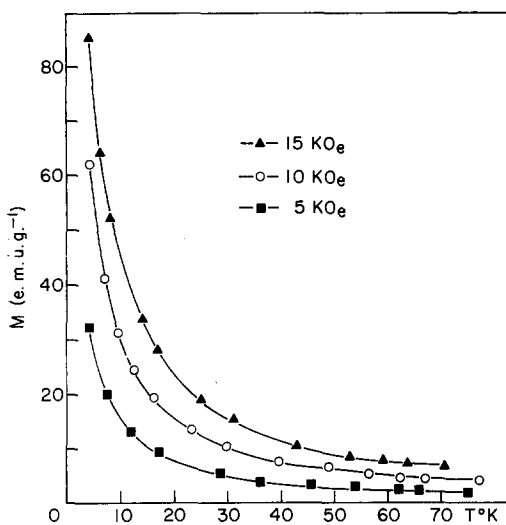


FIG. 6. Magnetic susceptibility vs temperature of  $\text{Eu}_5(\text{PO}_4)_3\text{Cl}$ .

TABLE IV

EFFECTIVE MAGNETIC MOMENTS  
OF EU(II) PHOSPHATES

Compound	$\mu_B$
$\text{Eu}_3(\text{PO}_4)_2$	8.3
$\text{Eu}_5(\text{PO}_4)_3\text{F}$	7.2
$\text{Eu}_5(\text{PO}_4)_3\text{Cl}$	7.2

compounds and their values appear in Table IV.

#### Infrared Data

Infrared spectra of the fluoride and chloride apatites were recorded. The absorption bands observed were at 580, 947, 1026 and 1070  $\text{cm}^{-1}$ , these being the characteristic phosphate bands in the corresponding Sr-apatites (14).

#### Discussion

The results obtained in this work confirm that apatites of divalent europium can be prepared. The divalency of the Eu cation was clearly proved by Mössbauer spectroscopy, the spectra showing the characteristic isomer shift of  $\text{Eu}^{2+}$  only. The crystallographic results have shown that the lattice dimensions of the compounds are close to those found for the corresponding isostructural Sr compounds (15, 16) an observation made also in case of sulfides, selenides, sulphates and carbonates of Eu (II) (17). This indicates the similarity in size of  $\text{Eu}^{2+}$  and  $\text{Sr}^{2+}$  and the similarity in their properties, and thus explains the formation of apatite-like compounds by divalent europium.

Magnetic susceptibility measurements show that Eu (II) phosphate is ordered below 5 K. No evidence was found about the magnetic ordering of the other compounds at temperatures above 4.2 K. The transition temperature found for  $\text{Eu}_3(\text{PO}_4)_2$  in this work confirms the paramagnetic Curie temperature reported for this compound (18); the  $\mu_{\text{eff}}$  was found higher in this work ( $8.3 \mu_B$ ) and closer to the theoretical value of  $\text{Eu}^{2+}$ , proving the complete divalency of Eu in  $\text{Eu}_3(\text{PO}_4)_2$ . The paramagnetic behavior and the  $\mu_{\text{eff}}$  values of the compounds support our findings that Eu is in the divalent state in the phosphates studied.

The results in the case of the solid solutions systems show that the substitution of Eu by Ca in the  $\text{Eu}_{5-x}\text{Ca}_x(\text{PO}_4)_3\text{F}$  system causes regular decrease in the lattice parameters; the points on Fig. 1 fall on a straight line. This system therefore follows Vegard's law, indicating the formation of continuous solid solutions. The situation is different in the systems where  $\text{Ba}^{2+}$  replaces  $\text{Eu}^{2+}$ . While the

structure in these systems remains apatite like, the lattice parameters change irregularly (Figs 2 and 3). The deviation from linearity in the expansion of the lattice, is most probably due to the relatively big difference in the size of the  $\text{Ba}^{2+}$  and  $\text{Eu}^{2+}$  ions. As a result of this difference, the cations are not randomly distributed between the triangle ( $M_{II}$ ) and column ( $M_I$ ) cationic positions. The irregular changes in the lattice parameters thus reflect the ordered occupation of the  $M_I$  and  $M_{II}$  positions by the  $\text{Ba}^{2+}$  and  $\text{Eu}^{2+}$  ions. Similar ordering was obtained in rare earth substituted Ba apatites (*I*). In this case the insertion of the smaller rare earth ions in the Ba apatites resulted in apatite like structures with symmetry different from the  $P6_3/m$  space group, because of ordering in the distribution of the cations among the  $M_I$  and  $M_{II}$  sites. The way of ordering in the solid solutions studied in this work could not be determined from our powder diffraction data and this must be further studied by single crystal methods.

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